

# Direct-Write Contacts for Solar Cells

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# Direct-Write Contacts for Solar Cells

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## ABSTRACT

We report on our project to develop inkjet printable contacts for solar cells. Ag, Cu, and Ni metallizations were inkjet printed with near vacuum deposition quality. Thick, highly conducting lines of Ag and Cu demonstrating good adhesion to glass, Si, and PCB have been printed at 100-200 °C in air and N<sub>2</sub>, respectively. Ag grids were inkjet-printed on Si solar cells and fired through silicon nitride AR layer at 850 °C resulting in 8% cells. Next-generation multicomponent inks (including etching agents) have also been developed with improved fire-through contacts leading to higher cell efficiencies. The approach developed can be easily extended to other conductors such as Pt, Pd, and Au, etc. In addition, PEDOT-PSS polymer-based conductors were inkjet-printed with the conductivity as good or better than those of spin-coated films.

## 1. Objectives

Inkjet printing is rapidly becoming a viable alternative to the existing deposition approaches for a variety of inorganic and organic electronic materials [1]. The inkjet effort at NREL is currently focused on metallic and polymer conductors. With appropriate inks, inkjet-printed metallizations can replace vacuum-deposited, screen-printed, and electroplated conductors in PV devices. Developing a low-cost, non-contact direct-write approaches such as inkjet printing for high-quality contacts directly contributes to achieving objectives of the Solar Energy Program for improved performance at reduced cost for PV devices.

## 2. Technical Approach

Organometallic compounds of Ag, Cu, and Ni in organic solvents (proprietary compositions) were used as the precursor inks for inkjet and spray printing of the metallic layers and patterns. The inks were printed in air or N<sub>2</sub> on various substrates including plastic, glass, and Si (Fig. 1).



Fig 1. Inkjet printhead positioned over a glass substrate.

Additional precursor inks (proprietary composition) were developed to provide for an etching agent, so as to facilitate firing through the SiN<sub>x</sub> AR coating in fritless Ag contacts. These precursors were inkjet-printed on SiN<sub>x</sub>-coated Si-ribbon p/n junctions provided by Evergreen Solar, Inc., and baked at various temperatures in order to optimize etching rate and profile. Glass-frit-containing nanoparticle based Ag inks provided by Ferro were also tested in our inkjet printer. Line patterns were printed with Ferro's inks onto AR-coated substrates provided by Evergreen Solar, Inc. and annealed in a rapid thermal processing (RTP) furnace. Both composition provided for good burn through and improved contact formation.

PEDOT-PSS polymer inks were printed on glass. Ink compositions and printing parameters, such as drop generation rate, drop ejection speed, and substrate temperatures, were varied in order to achieve the highest conductivities with satisfactory resolution and good morphological properties of the printed conducting patterns.

## 3. Results and Accomplishments

Metallic coatings printed from metalorganic inks had no detectable traces of carbon or oxides (Fig. 2).

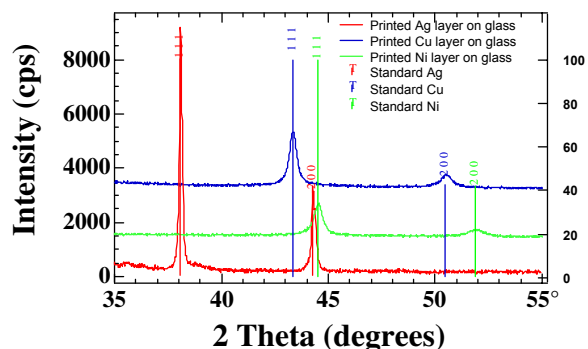


Fig 2. X-ray diffraction patterns of the spray-printed organometallic precursor inks.

A summary of important characteristics of the inkjet-printed contacts produced to date are presented in Table 1. Typical conductivities for the metallic coatings were: 2 μOhm.cm for Ag, 10 μOhm.cm for Cu and 100 μOhm.cm for Ni. Conductivity of the Ag layer is essentially that of the bulk metal, the Cu and Ni layers demonstrate approximately an order of magnitude higher resistivity than the bulk value. In general we found that the best results with Cu were obtained in inert atmosphere (N<sub>2</sub> or Ar). However, pure Cu coatings were obtained in air using rapid thermal processing. Similar conductivities were found for inkjet-printed metallic lines.

Table1. Important Characteristics of Printed Conductor Patterns

Material	Thick- ness ( $\mu\text{m}$ )	Line- width ( $\mu\text{m}$ )	Resistivity ( $\mu\Omega/\square\text{cm}$ )	Printing temperature ( $^{\circ}\text{C}$ )
Ag <sup>(1)</sup>	1- 15	100- 250	2	200
Ag <sup>(2)</sup>	1- 15	300- 600	7	250
Cu	1-15	200- 300	10	250
Ni	4		100	250
PEDOT: PSS	0.1	300	700	50-75
Fire- through agent	1-5	70- 200	NA	200

- (1) – Ag from metalorganic ink developed at NREL  
(2) – Ag from frit-containing nanoparticle ink (Ferro)

Improving the conductivity of printed Cu and Ni metallizations is an area of active investigation. Thick (up to 15  $\mu\text{m}$ ), highly conducting lines of Ag and Cu were printed on a variety of substrates, demonstrating good adhesion to glass, Si, and PCB (Fig. 3a,b).

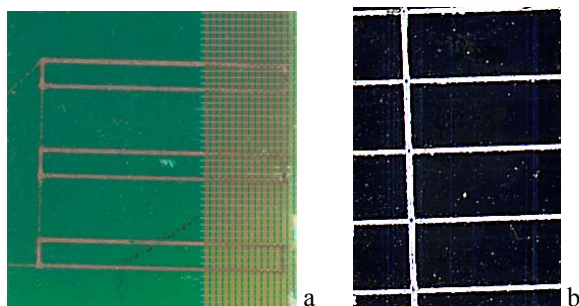


Fig. 3. 300- $\mu\text{m}$ -wide, 5- $\mu\text{m}$ -thick Cu lines printed on PCB in  $\text{N}_2$  at 200  $^{\circ}\text{C}$  (a); 250- $\mu\text{m}$ -wide, 10- $\mu\text{m}$ -thick Ag grids inkjet-printed on a Si solar cell in air at 200  $^{\circ}\text{C}$  (b).

Ag grids were inkjet-printed on Si solar cells and fired through a silicon nitride AR layer at 850  $^{\circ}\text{C}$ , resulting in 8% cells (Fig. 3b). Next-generation multicomponent inks (including surface modifying agents) have been developed for improved fire-through contacts, leading to higher cell efficiencies. These proprietary inks greatly improve the burn through and contact formation process.

A potentially significant advantage of inkjet printing is that with multi-layer printing it allows separate writing of a contact-formation layer, and then of the metal-forming layer, leading to more control of the contact-formation process and improved conductivity of the conductor lines. Figure 4 demonstrates a 70- $\mu\text{m}$ -wide, 1- $\mu\text{m}$ -deep pattern etched on a AR-coated Evergreen wafer by inkjet printing and consequent thermal processing at 750  $^{\circ}\text{C}$  for 10 min of an ink containing a proprietary etching agent.

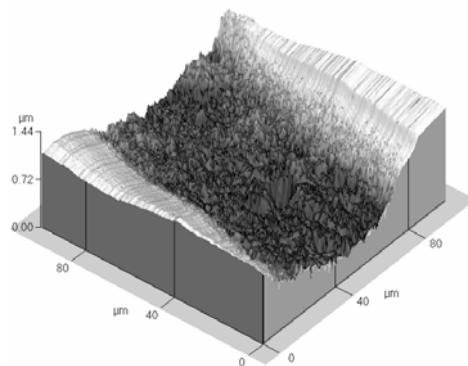


Fig. 4. 70- $\mu\text{m}$ -wide, 1- $\mu\text{m}$ -deep etch pattern produced by inkjet-printed “fire-through” agent in AR-coated Si wafer.

Complete burning through the  $\text{SiN}_x$  layer was observed at temperatures as low as 500  $^{\circ}\text{C}$ . Conventional, frit-containing nanoparticle Ag inks from Ferro were successfully inkjet printed resulting in 15- $\mu\text{m}$ -thick, 500- $\mu\text{m}$ -wide lines (Fig. 3b). Using these inks, ohmic contacts were achieved at much lower temperatures (650  $^{\circ}\text{C}$ –750  $^{\circ}\text{C}$ ) with a very short annealing cycle (less than a minute).

Organic solar cells and organic optoelectronics often rely on PEDOT-PSS as an organic transparent contact. Uniform PEDOT lines as narrow as 300  $\mu\text{m}$  were printed. Film roughness, thickness, conductivity, and work function were controlled by various parameters, including type of solvent, additives (DMSO), substrate temperature, addition of a surfactant, substrate cleaning, and settings of the inkjet. Films as thin as 100 nm, as smooth as 20 nm, and as conductive as 140 S/cm have been achieved. These conductivities are equal to the best conductivities achieved for spin-coated films. The value of the workfunction (by CPD) could be varied by as much as 0.5V.

#### 4. Conclusions

We have developed a set of tools and inks for the atmospheric direct-write deposition of various metals such as Ag, Cu, and Ni. Line widths, conductivities and thicknesses are comparable to, or better than, those produced by screen printing. We have shown how new inks can improve the contacting process for Si photovoltaics. We have demonstrated inkjet-printed patterns of highly conductive PEDOT polymer for contacts in organic photovoltaic cells. Future work will focus on improved resolution, multicomponent/multifunctional inks for enhanced contacts, improved inks for better conductivities of Cu and Ni metallizations, and integrating inkjet printing of metallic and organic contacts in device processing.

#### REFERENCES

- [1]. D. B. Wallace, W. R. Cox, and D. J. Hayes, in Direct-Write Technologies for Rapid Prototyping Applications, edited by A. Pique and D. B. Chrisey (Academic Press, 2002), p. 177.

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